Development of Magnesia Spinel brick using Pre-synthesized and in-situ spinel

A Thesis submitted in partial fulfillment of the requirements for the degree of

Bachelor of Technology in Ceramic Engineering

By

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Certificate

This is to certify that the work in this project entitled **"Development of Magnesia Spinel brick using pre-synthesized and in-situ spinel"** by **Amarjeet Kumar (110CR0416)** has been carried out under my supervision in partial fulfillment of the requirements for the degree of Bachelor in Technology during session 2013-14 in the Department of Ceramic Engineering, National Institute of Technology Rourkela, and this work has not been submitted elsewhere for a degree.

The candidate has fulfilled all the prescribed requirements.

Place: Rourkela

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ABSTRACT

This Project is about designing the Development of magnesia-spinel brick using pre-synthesized and in-situ spinel. The spinel's are a class of minerals of general formulation $A^{2+}B^{3+}{}_2O^{2-}{}_4$ which crystallize in the face centered cubic (isometric) crystal system, with the oxide anions arranged in a cubic close-packed lattice. The cation A fills the tetrahedral sites and cation B fills the octahedral sites. A and B are divalent and trivalent cations respectively.

Pre-synthesized spinel refractory is the refractory where the spinel material is synthesized separately and is then added into the brick composition. Where as in-situ spinel refractory is the refractory where the spinel forms inside the brick during the firing stages at higher temperatures.

The brick compositions of pre synthesized spinel and in-situ spinel were taken and pressed to form bricks. The bricks upon sintering at 1550^0C and 1600^oC led to increase in density. The in-situ spinel brick was found to have higher BD, lower porosity and higher shrinkage as compared to the pre synthesized spinel refractory brick.

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Chapter I

Introduction

1. Introduction:

Magnesium aluminate spinel ($MgAl_2O_4$) is an excellent refractory oxide of immense technological importance as a structural ceramic. It possesses useful physical, chemical and thermal properties, both at normal and elevated temperatures. Spinel can be used in formation of refractory bricks in combination with magnesia in two ways. In the first method pre-synthesized spinel is taken and mixed with magnesia. In the second method alumina is mixed with magnesia and it results in formation of in-situ spinel. There is great potential of this technology to be used as refractory lining because of its property of resisting high temperature.

Magnesia spinel is member of a group of oxides that have the same crystal structure, which named is spinel structure. The spinel group contains over twenty members, but only a few are considered common. The general formula of the spinel group is AB_2O_4.Where A represent a divalent metal in such as magnesium ion. And B represent trivalent metal ion such as aluminium. Spinel is the only compound a binary system magnesia and alumina. This powder upon sintering for 4h at 1600°C led to compacts with density as high as 92% with benign microstructural features.

1.1. Objective:-

The objective of this project is to distinguish between the properties of refractory bricks made by using magnesia and pre-synthesized spinel to that of refractory bricks made by use of alumina and magnesia which results in formation of in-situ spinel. The physical properties like apparent porosity and bulk density of both the types of bricks were compared with increasing

spinel and alumina percent. Apart from that the temperature effects on its properties are also measured. A phase analysis of the samples is also conducted by XRD to get detailed information about its structure.

1.2. Properties:-

Magnesia spinel is a highly refractory material, with a melting point of 2135^0C.

- If the amount of magnesia is higher than the magnesia content of pure spinel composition, then it is known as magnesia rich spinel (MR).
- If the amount of alumina is higher than the alumina content of pure spinel composition, then it is known as alumina rich spinel (AR). [9]
- Commercially there are many grades of spinal such as (MR 66, AR 78, AR 90) and by varying the composition [8].

Chapter 2

Background and Literature Review

2. Background and Literature Review

- **2.1 SPINEL:-**

- Spinel is the magnesium aluminum member of the larger spinel group of minerals. It has the formula $MgAl_2O_4$.[1]

- Its hardness is 8, its specific gravity is 3.58 and it is transparent to opaque with a vitreous to dull luster. It may be colorless, but is usually various shades of red, blue, green, yellow, brown, or black.$MgAl_2O_4$ spinel possesses high-melting point, high chemical inertness against both acidic and basic slags, low expansion values at elevated temperatures, and is an ecologically benign refractory material.[8]

- Various grades of magnesium-aluminate spinels are available commercially with different alumina and magnesia contents. Generally, MgO-spinel bricks are preferred for cement rotary kilns whereas Al_2O_3-spinel castables are preferred for steel ladles. The lifetimes of linings made of high purity alumina and magnesia are limited by their high wear rates arising from slag penetration and structural spalling.[8]

Magnesia:-

- Magnesia is a white hygroscopic solid mineral that naturally occurs as periclase.[9]
- Mgo is available as sintered and fused magnesia.
- All of it $MgCO_3$ is converted to MgO.
- The charge is +2 and it a divalent and its perfect missed with reactive alumina to making spinel.
- It is an alkaline earth's metal and the eighth-most-abundant element in the Earth's crust.[9]

- It has a melting point of 2852^0C and a boiling point of 3600^0C.
- It is widely used in refractory industry because of its properties which causes it to be stable at high temperatures.
- MgO is used as an insulator in industrial cables, as a basic refractory material for crucible and as a principal fire proofing ingredient in construction materials.[9]
- It has a density $3.58g / cm^3$ compound has high purity.[8]

Alumina:-

- It offers combination a good mechanical properties and electrical properties leading to a wide range application[11].
- Alumina can be produced in a range of purities with additives designed to enhance properties. A wide variety of ceramic processing methods can be applied to produce a wide variety of sizes and shapes of components. In addition it can be readily joined to metals or other ceramics using metallizing and brazing techniques. Alumina based ceramics are by far the largest range of advanced ceramics made by Morgan Technical Ceramics. [7]

Due to the important combination of properties, the behavior and characteristics of possible component. Typical Alumina characteristics include:

- Good strength and stiffness.
- Good hardness and wear resistance.
- Good corrosion resistance.
- Good thermal stability excellent dielectric properties.
- Low dielectric constant Low loss tangent.[9]

- Typical Alumina applications include: Refractory, Seal rings, Medical prostheses Laser tubes, Electronic substrates, Ballistic armour, Thermocouple tubes, Electrical insulators, Grinding media, Thread guides and Wear components.

Magnesia Aluminate Spinel ($MgAl_2O_4$):-

Properties:-

- Magnesium aluminate spinel is a member of a group of oxides that have the same crystal structure, which is named the spinel structure. The spinel group contains over twenty members, but only a few are considered common. The general formula of the spinel group is AB_2O_4, where A represents a divalent metal ion such as magnesium, iron, nickel, manganese and/or zinc, and B represents trivalent metal ions such as aluminum, iron, chromium or manganese. Unless otherwise described, the term "spinel" in this paper will refer to $MgAl_2O_4$, the mineral spinel, which is the only compound in the binary system MgO – Al_2O_4.[2]

- A strong feature of this group of minerals is the tendency for substitution solid solutioning, where large percentages of one or both of the spinel components may be substituted by others of the group without modification of the crystal structure, or indeed any significant strain on the crystal lattice. Both magnesium and aluminum cations can be replaced by others with similar size, keeping the electrochemical balance. Thereby a wide range of solid solutions results for the spinel group members.[10]

- $MgAl_2O_4$ structure shows an increasing phase region with increasing temperature, especially towards higher alumina contents.

Physical properties:-

- Magnesium aluminate spinel is a highly refractory material, with a melting point of 2135°C. a comparison of the density, thermal expansion coefficient and thermal conductivity of the end-members (MgO and Al2O3) compared to the spinel phase.
- It differences between these phases in thermal expansion are responsible, in part, for the superior thermal shock resistance of spinel.

- Thermal and physical properties a spinel, Mgo and Al_2O_3:

	Spinel ($MgAl_2O_4$)	Periclase (MgO)	Corundum (Al_2O_3)
Density (g/cm^3)	3.58	3.58	3.99
Thermal conductivity(W/mK)	5.90	7.10	6.30
Thermal coefficient of expansion	7.60	13.50	8.80

From the above table we get a comparison of the density, thermal expansion coefficient and thermal conductivity of the end members (MgO, Al_2O_3) compared to the spinel phase. The difference between these phases in thermal expansion is responsible, in part, for the superior thermal shock resistance of spinel. [5]

Advantages

The main advantages of using Magnesia Spinel bricks in cement kilns are summarized in the following points:-

- Low thermal expansion coefficient of magnesia spinel bricks.
- High resistance to thermo-mechanical stress.
- High resistant to corrosion and changes in kiln atmosphere.
- Low content of secondary oxides which results in mineral alteration in structure of the hot face in service.
- Elimination of chromite, which makes the bricks less susceptible to alkali attack in service.

The young modulus decreased significantly with increasing sintering temperature which is converse to the trend declared by that in situ formed spinel. Spinel particles are added in various proportions to MgO in order to improve its thermal shock resistance. The reason for improvement in thermal shock resistance is linked to the large difference in thermal expansion coefficient between magnesium oxide (mean value $\approx 13.5\times10^{-6}\ {}^{0}C^{-1}$) spinel ($\approx 7.6\times10^{-6}\ {}^{0}C^{-1}$). When the dispersed particle size is large than

critical value MgO-spinel composite with $\alpha_{spinel} < \alpha_{MgO}$ show low strength because the radial crack produced readily link together. [6]

Application of magnesia spinel refractory: -

Spinel applications are impact pads, purging cones and well blocks, nozzles, wears and dams, lances, and slide gates. Other spinel applications to be mentioned are glass refractories. However, here stoichiometric spinel compositions are preferred. [9]

Magnesium aluminate spinel has been recognized as one of the effective refractory materials and used in various applications such as, cement rotary kilns, vacuum induction furnaces, continuous casting tundishes, degasser snorkels and lances, glass industries,etc. $MgAl_2O_4$ spinel possesses high-melting point, high chemical inertness against both acidic and basic slags, low expansion values at elevated temperatures, an is an ecologically benign refractory material.

Chapter 3

Experimental

3. Experimental:-

3. 1.Grade and selection of material

- MgO is taken from fused magnesia.
- The periclase structure of the magnesia will prevent the formation of hydrate of magnesia.
- It has no tendency for formation of hydrate due to preclase structure.
- All of its $MgCO_3$ is converted to MgO.[8]

- Reactive alumina is taken because of the following reasons:-
- It has high surface area.
- It will react with MgO well.
- Spinel taken is of grade AR78.[9]

Size of the materials used:-

1. Fused MgO

   Coarse size: 1-3 mm
   Medium size: 0-1 mm
   Fine size: < 200μm

2. Spinel

   Medium Size: 0.5-1 mm

3. Alumina

   Fine Size: < 75μm

The above mentioned materials were taken in different composition to make 6 batches of sample. For each batch 4 bricks were made. The composition of different batches is mentioned in the following pages.
It will consist of two compositions mainly which are as follows:-

- Pre-synthesized spinel – In this type of sample preparation spinel used is pre-synthesized which is AR78 in the given case and the bricks formed by this method on mixing with magnesia is known as pre-synthesized body.

- In-situ spinel- In this type of sample preparation alumina and magnesia are mixed in a specified proportion which on sintering gives rise to formation of in-situ spinels.

- **Composition of different batches of sample**

Batch 1

S.No.	Materials	Size	Weight(gm)
1.	Fused MgO	1-3 mm	45
2.	Spinel	0.5-1 mm	10
3.	Fused MgO	<75μm	45

Batch 2

S.No.	Materials	Size	Weight (gm)
1.	Fused MgO	1-3 mm	35
2.	Spinel	0.5-1mm	20
3.	Fused MgO	<75 µm	45

Batch 3

S.No.	Materials	Size	Weight(gm)
1.	Fused MgO	1-3 mm	25
2.	Spinel	0.5-1 mm	30
3.	Fused MgO	<75µm	45

Batch 4

S.No.	Materials	Size	Weight(gm)
1.	Fused MgO	1-3 mm	45
2.	FM	0.5-1 mm	10
3.	FM	<75µm	37.8
4.	Alumina (CTaFG)	Fine	7.2

Batch 5

S.No.	Materials	Size	Weight(gm)
1.	Fused MgO	1-3 mm	45
2.	FM	<1 mm	10
3.	FM	Fine	30.6
4.	Alumina	Fine	14.4

Batch 6

S.No.	Materials	Size	Weight(gm)
1.	Fused MgO	1-3mm	45
2.	FM	<1mm	10
3.	FM	Fine	23.4
4.	Alumina	Fine	21.6

Processes:-

- Spinel: it is in form of medium particle. It didn't any calcination and the size is (0.5-1mm). Spinel it has already been made. Its scientific name is AR90. It will react with fused magnesia in coarse, medium and fine types. It will consist three batches.

- Alumina: reactive alumina in powder (fines) form, it didn't need any calcination. The size is <75 um.

- Fused magnesia: it is three types coarse, medium and fine. And coarse types has a high surface area.it will react alumina and spinel, consist of SIX BATCHES. And different amount will become of the all batches composition. Each batch will have different composition.

Mixture Preparations:-

For each batch: 200gm of total mixture was to be prepared. Hence, fused magnesia and sized (1-3mm) coarse particle use. The amount of 45gm.then spinel use and size (medium 0.5-1mm) as the amount of 10gm and fused magnesia (<75um) of 45gm is the total mixed in dry condition. Then to it 4% binder was added to it and left for ageing. Two shapes were prepared from each 100gm batch.

Pressing:-

- The mixture is filled in die of 65×35mm.

- Than the filled about 50gm of powder to it pressed at 9 Ton for Dwelling time of 30second.

- Then the mould is cleaned with acetone and again with steric acid for lubrication and pressed again.

- This cycle is repeated for making about 24 bricks or 6 batches.

Fig: 1. Hydraulic Pressing machines

Drying:-

- The pressed samples were then kept in dryer for 24 hours at 110^0C to remove and moisture present in it.

- It is done carefully to remove moisture without formation of crack.

Firing:-

- The firing of the samples was done at 1550 and 1600^0C and heating rate of 3^0C/minute was used.

- All firings were done for a soaking time of 120 min at the peak temperatures.

Fig: 2. Dryer machine and Heating Furnace

CHAPTER 4

Results and Discussion

Results and Discussion:-

Green Body Dimension- The dimension of the body after pressing and before firing is called the green body dimension.

Following were the dimension of different samples of green body:

Batch 1

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	10.18	30.14	65.22
D	12.04	13.18	65.25
B	9.69	30.14	65.22
C	8.56	30.15	65.21

Batch 2

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	10.07	30.11	65.36
D	8.71	30.27	65.45
B	9.43	30.52	65.26
C	10.43	30.27	65.45

Batch 3

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	10.84	30.17	65.20
D	9.89	30.23	65.23
B	10.10	30.23	65.23
C	10.98	30.19	65.20

Batch 4

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	9.69	30.15	65.09
D	9.31	30.15	65.15
B	10.18	30.14	65.12
C	8.26	30.26	65.09

Batch 5

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	8.39	30.27	65.19
D	9.01	30.17	65.18
B	12.93	30.13	65.14
C	8.59	30.13	65.19

Batch 6

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	9.01	30.21	65.15
D	9.74	30.23	65.15
B	10.84	30.17	65.15
C	8.45	30.11	65.14

The Dimension of samples after firing (A and D at 1550^{0}C while 'B' and 'C' at 1600^{0}C)

Batch 1

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	10.07	30.10	65.12
D	11.90	30.14	65.14
B	9.88	30.15	65.06
C	8.50	30.19	65.08

Batch 2

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	9.96	30.15	65.00
D	8.68	30.07	65.08
B	9.42	30.22	64.85
C	10.30	30.16	65.05

Batch 3

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	10.75	30.15	64.87
D	9.85	30.14	64.78
B	10.05	30.12	64.75
C	10.91	30.14	64.66

Batch 4

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	9.54	30.05	65.02
D	9.17	30.09	65.02
B	10.02	30.04	64.80
C	8.13	30.15	64.88

Batch 5

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	8.30	30.12	65.11
D	8 .74	30.08	65.09
B	12.74	30.05	65.07
C	8.49	30.02	64.80

Batch 6

Sample name	Height(mm)	Breadth(mm)	Length(mm)
A	8.90	30.08	65.01
D	9.44	30.07	65.09
B	10.71	30.01	64.93
C	8.47	29.99	64.84

Bulk Density and Apparent porosity:

Bulk Density

It is the dimensional density of the sample. It means its volume and mass ratio.

B.D = **(W_d X Density of water) / (W_{soaked}- $W_{suspended}$)**

- Where density of water is taken as $1gm/cm^3$.

Apparent porosity

Apparent porosity referred to the amount of surface pores (density removing surface pores). It is calculated by the formula:-

Apparent porosity = $(W_{soaked}-W_{dry}) / (W_{soaked}-W_{suspended})$ X 100

- **Methodology**

Boiling method:-

1. The sample is taken and cut into small pieces and the dry weight of the specimen is taken.

2. The sample is then immersed in water and boiled for two hours.

3. The suspended and soaked weights are taken after boiling.

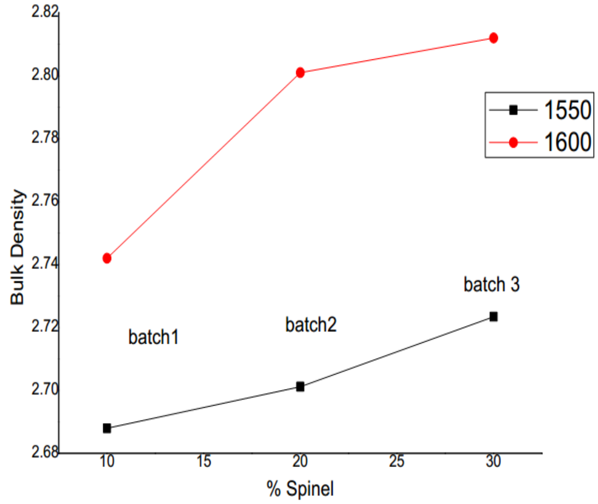

Fig.4. Bulk density Vs Spinel%

From this graph we can observe that the bulk density at higher temperature (i.e. 1600^0C) is higher than that at 1550^0C. As well as we also see that with increasing percent of spinel in the composition the bulk density also increases at both the temperature.

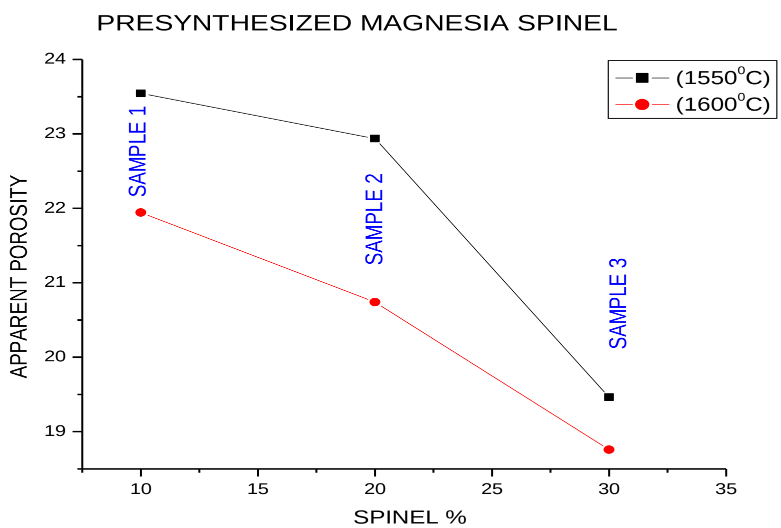

Fig.5. Apparent porosity Vs Spinel%

From this graph we observe that the apparent porosity at 1600^0C is lower than that at 1550^0C. Hence we can conclude that higher temperature is better for refractory bricks formation. Secondly, we also see that with increasing spinel percentage the apparent porosity decreases significantly.

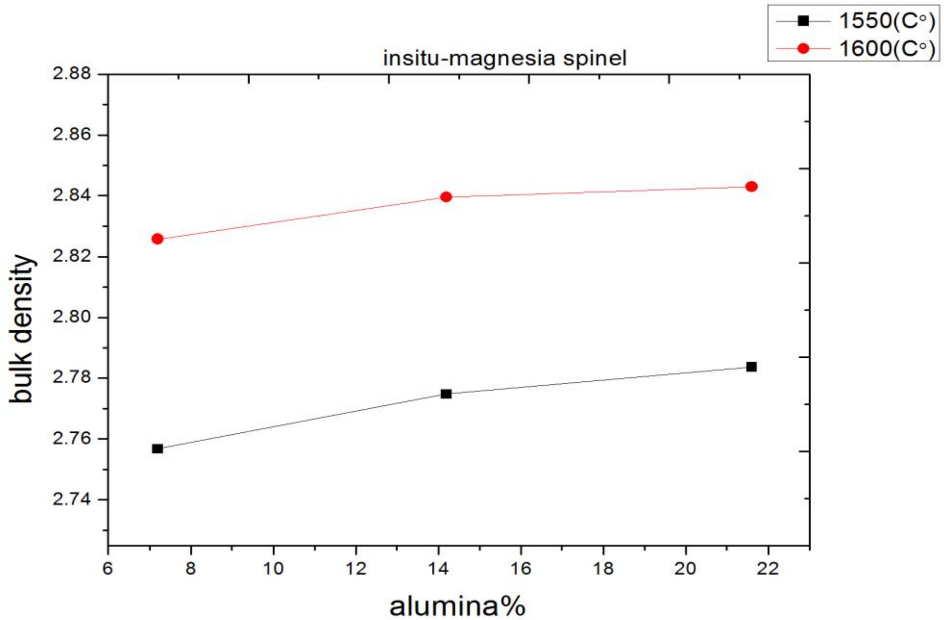

Fig.6. Bulk Density vs Alumina%

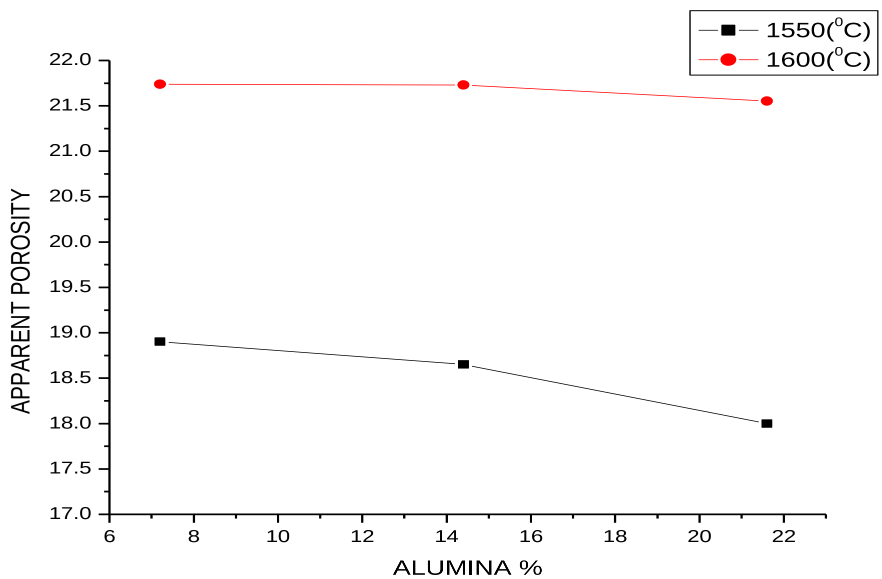

Fig.7. A.P vs Alumina%

From the graphs of apparent porosity and bulk density against alumina percent we observe the same trends as observed with pre-synthesized spinel which is better physical properties at a higher temperature.

- %Volume shrinkage = (V_i -V_f / V_i)*100

V_i = Volume before firing.

V_f =Volume after firing.

- %Linear shrinkage = (L_i –L_f /L_i)*100

L_i =Length before firing.

L_f =Length after firing.

Avg. Volume shrinkage =1.443

Avg. Linear shrinkage = 0.240

- **XRD (X-Ray Diffraction) Analysis:-**

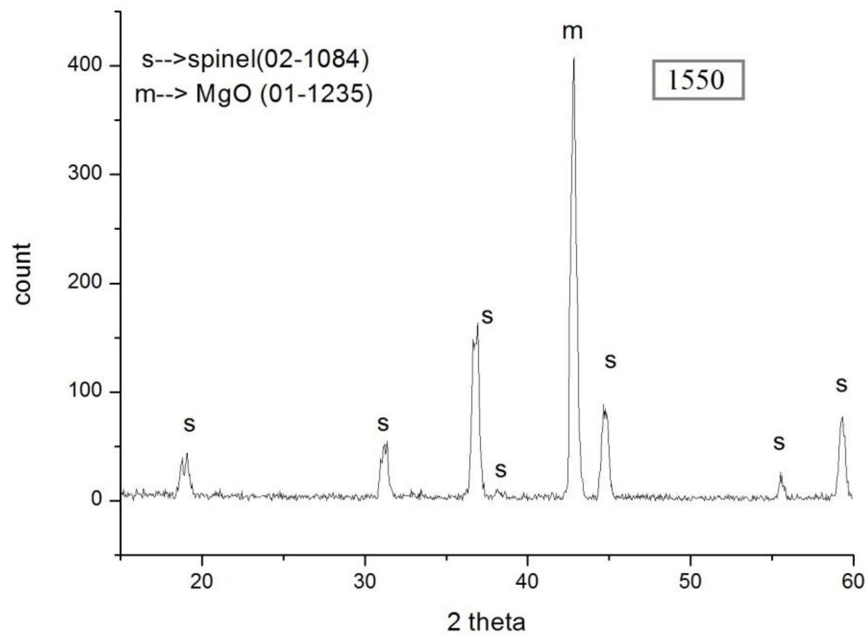

Fig.8.XRD of 14.2 wt% Al2O3 containing batch sintered at 1550^{0}C

From the graph we see that the percentage of magnesia is more than that of spinel in the total mixture.

Chapter 5

Conclusion

Conclusion

Magnesia spinel brick was prepared which can be recognized as one of effective refractory materials and can be used in various application such as Cement rotary kilns, Vacuum induction furnace, Continuous casting tundishes, Glass industry for its property of high melting point, Low Expansion, Shrinkage, Increase in strength with increase in temperature as Bulk density increases and Porosity decreases with temperature rise.

From the graphs we also conclude that physical properties attained in case of refractory bricks where in-situ formation of spinel took place is better than that of pre-synthesized spinel.

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